

# Many-body calculations of relativistic energy shifts for single- and double-valence atoms

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Relativistic Hartree-Fock method together with many-body perturbation theory and configuration interaction techniques are used to calculate relativistic energy shifts for frequencies of the strong electric dipole transitions of C III, C IV, Na I, Mg I, Mg II, Al II, Al III, Si IV, Ca II and Zn II. These transitions are used for search of the variation of the fine structure constant in quasar absorption spectra. The results are in good agreement with previous calculations. The analysis of Breit contributions is also presented.

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## I. INTRODUCTION

Search for variation of fundamental constants is currently an extensive area of research which spans the whole lifetime of the Universe from Big Bang nuclear synthesis to present day atomic-clock experiments (see, e.g. a review by Uzan [1]). This search is motivated by theories unifying gravity with other interactions as well as by many cosmological models. In both cases a possibility for fundamental constants to vary in space and/or time is present.

Strong evidence that the fine structure constant,  $\alpha$  might be smaller about ten billion years ago was found in the quasar absorption spectra [2, 3, 4, 5, 6, 7]. This result was obtained from the analysis of the data from Keck telescope in Hawaii by the group of researchers based at University of New South Wales in Australia. However, the analysis of the data from VLT telescope in Chile performed by different groups [8, 9] gives null result. There is an outgoing debate in the literature about possible reasons for this disagreement.

All the analysis in Refs. [2, 3, 4, 5, 6, 7, 8, 9] was performed with the use of the so-called many-multiplet (MM) method which was first suggested in Refs. [2, 10]. This method uses frequencies of strong atomic electric dipole transitions for the analysis. Its sensitivity to variation of the fine structure constant is more than an order of magnitude better than the analysis of the fine structure intervals which was used before [11, 12, 13]. This dramatic gain in sensitivity comes with some complications. The method relies on atomic calculations to reveal dependence of atomic frequencies on the fine structure constant. All calculations used in the analysis so far were performed within a single group of researches bases at the University of New South Wales [14, 15, 16, 17, 18, 19].

Due to importance of detecting of any variation of fundamental constants and controversy of the results it is important that atomic calculations be also verified by independent calculations.

A positive development in this direction is the recent independent calculation of the relativistic energy shifts in Fe II ion [20]. Fe II is a single most important element for the analysis of quasar absorption spectra. It has lines which move in opposite direction if  $\alpha$  varies, and the value of this shift is relatively large. In principle, subject to sufficient statistics, it alone can serve as a probe of variation of the fine structure constant in quasar absorption spectra [20]. However, calculations for Fe II are difficult due to large number of valence electrons.

In present work we perform further verification of the relativistic energy shifts in atoms of astrophysical interest by considering atoms and ions with one and two valence electrons. In the case of single-valence electron atoms we use Dirac-Hartree-Fock method (DHF) and relativistic many-body perturbation theory (RMBPT). For double-valence electron atoms we use DHF, RMBPT and configuration interaction (CI) technique. The results on this stage of calculations are in very good agreement with previous calculations.

We also perform the analysis of role of Breit interaction. It turns out that Breit contribution to the energies and relativistic energy shifts are small. However, Breit interaction gives significant contribution to the fine structure intervals bringing them to excellent agreement with experiment. Therefore, inclusion of Breit contributions is important for the analysis of the accuracy of calculations.

## II. METHOD

### A. q-factor calculations

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The difference between frequencies in QSO spectra and

in the laboratory after taking into account the Doppler shift depends on values of fine-structure constant  $\alpha$ . For small changes of  $\alpha$ , the transition frequency changes linearly with  $(\alpha/\alpha_0)^2$  and can be presented in a form

$$\omega(x) = \omega_0 + qx, \quad (1)$$

where  $\omega_0$  is the laboratory value of the frequency and  $x = (\alpha/\alpha_0)^2 - 1$ ,  $q$  is the sensitivity coefficient to be found from atomic calculations. Note that

$$q = \frac{d\omega}{dx} \text{ at } x = 0. \quad (2)$$

To obtain  $q$ -factors theoretically, it is necessary to calculate energies for at least two different values of the fine structure constant. Symmetric formula for the derivative is more accurate, and better precisions of  $q$  can be reached by calculating energies at two values of  $\alpha$  symmetrically displaced from the standard value. Due to numerical accuracy issues and non-linear dependence in a large range, the displacement should be not very small and not very large. We find that  $\alpha_1 = 1/134.0$  and  $\alpha_2 = 1/140.0$  satisfy both conditions. The  $q$  values are calculated using the following equation

$$q = [E(\alpha_1) - E(\alpha_2)]\alpha_0^2/(\alpha_1^2 - \alpha_2^2), \quad (3)$$

The energies and  $q$ -factors are both in inverse cm units.

### B. DHF and 2nd-order RMBPT

For  $q$ -factors of univalent atoms and ions, we calculate energies using the 2nd-order RMBPT formalism built on expansion in the frozen-core  $V^{(N-1)}$  DHF basis. By comparison of  $q$ -factors from the 2nd-order and DHF calculations, we find that the precision of second-order theory is expected to be sufficient. The 2nd-order RMBPT formalism is described in Ref.[21]. In the DHF basis first-order correction is already included, and the number of second-order corrections is reduced. The summation over excited states in the second-order expressions is carried out by using a finite compact B-spline DHF basis, with cavity sizes chosen to minimize influence of boundary conditions on the valence energies of interest. Angular orbital momentum of excited states is limited to 5, without much reduction in the precision. Other parameters are chosen to minimize numerical errors.

The second-order RMBPT gives much more accurate energies than the DHF theory as can be seen from our calculations presented in Table I. We also compare theoretical and experimental fine-structure splitting between  $p_{3/2}$  and  $p_{1/2}$  states. The agreement is very good in the second-order of RMBPT. However, it is further significantly improved when the Breit corrections discussed in next section are added. This is another indication of high accuracy of the calculations.

TABLE I: DHF and 2nd-order energies and fine-structure splittings of univalent atoms/ions

Element	State	Energy			Fine Structure		
		DHF	E2 <sup>a</sup>	Expt <sup>b</sup>	E2 <sup>a</sup>	E2+Br <sup>c</sup>	Expt <sup>b</sup>
C IV	2p <sub>1/2</sub>	65201	64548	64484			
	2p <sub>3/2</sub>	65328	64680	64592	132	107	108
Na I	3p <sub>1/2</sub>	15921	16812	16956			
	3p <sub>3/2</sub>	15937	16831	16973	18	17	17
	4p <sub>1/2</sub>	28904	30068	30267			
	4p <sub>3/2</sub>	28909	30074	30273	6	6	6
Mg II	3p <sub>1/2</sub>	34530	35603	35669			
	3p <sub>3/2</sub>	34620	35700	35761	97	91	92
	4p <sub>1/2</sub>	78574	80463	80620			
	4p <sub>3/2</sub>	78605	80496	80650	32	30	31
Al III	3p <sub>1/2</sub>	52709	53672	53683			
	3p <sub>3/2</sub>	52944	53919	53917	247	233	234
	4p <sub>1/2</sub>	141252	143538	143633			
	4p <sub>3/2</sub>	141334	143623	143714	85	80	80
Si IV	3p <sub>1/2</sub>	70540	71309	71288			
	3p <sub>3/2</sub>	71008	71794	71749	486	461	461
	4p <sub>1/2</sub>	215704	218226	218267			
	4p <sub>3/2</sub>	215870	218397	218429	171	162	162
Ca II	4p <sub>1/2</sub>	23403	25490	25192			
	4p <sub>3/2</sub>	23603	25722	25414	232	225	223
Zn II	4p <sub>1/2</sub>	44610	48548	48481			
	4p <sub>3/2</sub>	45347	49429	49355	881	866	874

<sup>a</sup>DHF+2nd-order

<sup>b</sup>NIST, Ref. [31]

<sup>c</sup>E2+Breit (see Table II)

### C. Breit corrections

Relativistic energy shift which was considered above is due to the difference between Dirac and Schrödinger equations. This difference leads to a correction to the energy proportional to  $\alpha^2$  in the leading order. Therefore, for small change of  $\alpha$  this correction coincides with the definition of the  $q$ -coefficient (see formula (1)). However, there is also Breit relativistic correction to the inter-electron interaction [22]. This correction is also proportional to  $\alpha^2$  and therefore contributes to the  $q$ -coefficients. It is important to check the values of these corrections to have reliable results. We include Breit interaction using the technique developed in our previous works [23, 24].

We use the following form of the Breit operator (atomic units)

$$\hat{H}^B = -\frac{\hat{\alpha}_1 \cdot \hat{\alpha}_2 + (\hat{\alpha}_1 \cdot \hat{\mathbf{n}})(\hat{\alpha}_2 \cdot \hat{\mathbf{n}})}{2r}. \quad (4)$$

Here  $\mathbf{r} = \hat{\mathbf{n}}r$ ,  $r$  is distance between electrons and  $\hat{\alpha}_i$  is the  $\alpha$ -matrix of the corresponding electron. This is a low frequency limit of the relativistic correction to the Coulomb interaction between electrons. It contains magnetic interaction and retardation.

Similar to Coulomb interaction, Breit interaction creates a potential which is to be added to Hartree-Fock potential. In the case of closed-shell atoms direct term

in Breit potential vanishes and only exchange term remains. This is the case for single-valence-electron atoms considered in present work since we use the  $V^{N-1}$  approximation.

Self-consistent calculations are performed for a closed-shell core in a potential which is a sum of Coulomb and Breit terms

$$\hat{V} = \hat{V}^C + \hat{V}^B. \quad (5)$$

States of valence electrons are calculated in the same potential (5). In this approach Breit interaction between electrons receives exactly the same treatment as the Coulomb one. It is first included as interaction between core electrons and then as an interaction between valence and core electrons. Therefore, an important effect of core relaxation is included. A less important effect of Breit interaction on inter-electron correlations is not included in present work. This is justified by small value of the corrections.

Note that non-perturbative treatment of Breit interaction leads to inclusion of higher-order in Breit operator terms, terms proportional to  $(\hat{H}^B)^2, (\hat{H}^B)^3$ , etc. Inclusion of these terms cannot be justified and in principle they can be easily eliminated by a rescaling procedure in which Breit operator is suppressed in the calculations by a scaling parameter  $\lambda$  and then the answer is interpolated to  $\lambda = 1$ . It turns out, however, that as a rule  $\lambda = 1$  is already in linear regime.

The values of the corrections are found by running programs with and without corresponding extra terms in the potential. The calculated values are presented in Table II. In Table I we also included Breit corrections to the fine structure splitting.

Calculations show that although first-order valence Breit correction is a dominant contribution among Breit corrections to the energy of valence electrons, transition energy has a substantial cancelation for this correction, and Breit core-relaxation contribution becomes comparable with the valence Breit contribution for the transition energies and hence for  $q$ -values. The inclusion of core-relaxation effect significantly changed the value of Breit contribution.

#### D. BO+CI method

To calculate alpha variation coefficients for divalent atoms and ions, we will use the Brueckner-orbital (BO)+CI method, introduced in Ref.[25], and modified in Ref.[26] to include first-order Breit corrections. This method is essentially the combination of CI, to treat strong valence-valence interactions, and MBPT, to treat important valence-core interactions. It is similar to the method discussed in Refs.[27, 28, 29].

The BO-CI method described in detail in Ref.[25] is based on the effective Hamiltonian formalism which leads to the problem of diagonalization of the Hamiltonian matrix built on the two-electron configuration

TABLE II: Calculations of  $q$ -factors for univalent atoms/ions

Atom/Ion	State	DHF+2nd	Breit	Total	Other <sup>a</sup>
C IV	3p1/2	102	13	115	104(20)
	3p3/2	233	-12	221	232(20)
Na I	3p1/2	45	-1	44	45(4)
	3p3/2	63	-2	61	63(4)
	4p3/2	59	-2	57	59(4)
	4p1/2	53	-2	51	53(4)
Mg II	3p1/2	119	1	120	120(10)
	3p3/2	216	-5	211	211(10)
	4p1/2	167	-6	161	
	4p3/2	200	-8	192	
Al III	3p1/2	218	5	223	216(14)
	3p3/2	466	-9	457	464(30)
	4p1/2	349	-12	337	
	4p3/2	434	-17	417	
Si IV	3p1/2	347	13	360	346
	3p3/2	835	-12	823	862
	4p1/2	617	-20	597	
	4p3/2	789	-29	760	
Ca II	4p1/2	219	3	222	224
	4p3/2	454	-4	450	452
Zn II	4p1/2	1590	-5	1585	1584(25)
	4p3/2	2508	-20	2488	2479(25)

<sup>a</sup>Ref. [30]

TABLE III: Calculations of  $q$ -factors for divalent atoms/ions

Atom/Ion	State	CI+MBPT	Breit	Total	Other <sup>a</sup>
C III	2s2p			163	165
Mg I	3s3p	93	-7	85	86(10)
	3s4p	89	-8	80	87
Al II	3s3p			270	270(30)

<sup>a</sup>Ref. [30]

state functions. Beyond the frozen-core Hamiltonian the first-order electron-electron interaction Hamiltonian and second-order correction which consists of the two-particle screening correction and the one-particle self-energy correction are included. In the BO-CI method, the basis functions are chosen as BO and include second-order self-energy corrections together with DHF potential. The residual two-particle Hamiltonian matrix, that includes first-order valence-valence interaction and second-order Coulomb screening interaction, is evaluated in the BO basis and diagonalized to obtain state energies and CI wave functions.

### III. RESULTS

Results of calculations of  $q$ -factors for univalent and divalent atoms and ions are presented in Tables II and III, respectively. Accurate agreement is achieved between our second-order values and  $q$ -factors previously reported and compiled in Ref.[30]. Univalent atoms and ions are calculated from second-order RMBPT energies with the method described in the previous section. Because the

contribution from the second order turned out to be relatively small, we expect that second-order results will give quite reliable values. Because previously only dominant relativistic effects were included within DHF formalism, we also added Breit corrections to energies to investigate the effects beyond Dirac-Fock approximation.

For divalent atoms and ions calculations are performed with the BO+CI code, which is described in the previous section. All first-order Breit corrections introduced into CI+MPBT in Ref.[26] are also included.

#### IV. CONCLUSIONS

We have calculated  $q$ -factors for mono- and divalent atoms and ions of interest for the extraction of fine-

structure variation from quasar spectra. Our results agree with good accuracy with previous calculations and provide necessary independent verification. In particular, more difficult for theory divalent atoms and ions are calculated with a new method, BO+CI. Breit corrections, ignored previously, have been also evaluated. Although found in this work to be small, potentially they constitute a dominant class of relativistic corrections beyond the Dirac-Fock formalism.

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